

PATENT SPECIFICATION

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(54) BONDING PROCESS USING POLYURETHANE MIXED ADHESIVES

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

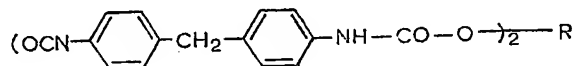
This invention relates to a bonding process using polyurethane mixed adhesives. It is known to produce mixed adhesives from hydroxyl polyesters and polyisocyanates. These mixed adhesives are used for bonding wood, stoneware, metal and other materials with high cohesive forces. A disadvantage of these adhesives is their high viscosity, which frequently makes it necessary to add a solvent. Moreover, bonds produced with adhesives based on hydroxyl polyesters and polyisocyanates are subject to hydrolysis with the result that they lose their strength prematurely.

It has now been found that mixed adhesives for use in a bonding process which are distinguished by exceptionally high strength and rapid setting can be produced from certain polyalkylene polyether polyols, certain solvent-free polyisocyanates and suitable catalysts. These adhesives have a low viscosity and the added advantage of being physiologically substantially harmless due to the absence of volatile components, such as solvents or volatile polyisocyanates. Bonds produced from such adhesives are not subject to hydrolysis and are therefore much more stable. In addition, the bonds have substantially higher flexibility at low temperatures.

It has been proposed in our British Patent No. 1,382,357 to use mixtures based on polyalkylene polyether polyols (having a molecular weight in the range of from 1000 to 10,000) and certain diisocyanatodiurethanes for producing layers of contact adhesives. The suitability of these systems for the production of layers of contact adhesives is due mainly to the relatively high molecular weight of the polyether polyols used there. The systems are less suitable for mixed adhesives which make it possible for bonds with high cohesive strengths to be produced.

This invention provides a process for bonding together materials in which a mixed adhesive comprising:

- 1a) at least one polyalkylene polyether polyol of molecular weight from 300 to 1999;
- 1b) 0—150 mols %, based on component 1a, of at least one polyalkylene polyether polyol of molecular weight from 2000 to 6000;
- 2a) at least one diisocyanatodiurethane corresponding to the following general formula:



wherein R represents a radical obtained by removing the hydroxyl groups from a glycol having a molecular weight of from 62 to 400;

2b) 0—800 mols %, based on component 2a, of 4,4'-diisocyanatodiphenylmethane; and

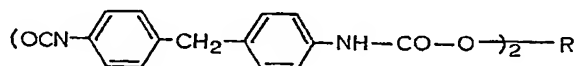
3) a catalyst for accelerating the OH/NCO reaction; the ratio of (1a+1b)+(2a+2b) corresponding to an NCO/OH ratio of from 0.5 to 2.5, is applied to the material and the bonds are fixed by the application of pressure.

Mixtures particularly suitable for use according to the bonding process of the invention are those which contain polyalkylene polyether polyols within the molecular weight range of from 300 to 1999 and preferably from 400 to 999 as the sole polyalkylene polyether polyol component.

This invention therefore also relates to the use of a mixture containing:

1) at least one polyalkylene polyether polyol with a molecular weight of from 300 to 1999;

2a) at least one diisocyanatodiurethane corresponding to the following general formula:



wherein R represents a radical obtained by removal of the hydroxyl groups from a glycol having a molecular weight of from 62 to 400;

2b) 0—800 mols %, based on component 2a, of 4,4'-diisocyanatodiphenylmethane, components 1) 2a) and 2b) being used in quantities corresponding to an NCO/OH ratio of from 0.7 to 2.0; and

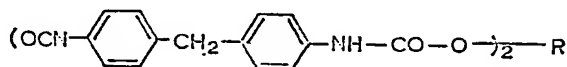
3) a catalyst for accelerating the OH/NCO reaction.

The polyalkylene polyether polyols mentioned under 1a) have a molecular weight of from 300 to 1999, preferably from 400 to 999.

The polyalkylene polyether polyols mentioned under 1b) have a molecular weight of from 2000 to 6000, preferably from 2500 to 4000.

These polyether polyols may be obtained by known processes of reacting alkylene oxides with suitable starter molecules, such as amines or, in particular, water or low molecular weight (62—400) alcohols which are at least dihydric, such as ethylene glycol, propylene glycol, butylene glycol, glycerol, trimethylol propane and hexane triols. Suitable alkylene oxides are, in particular, ethylene oxide, propylene oxide and butylene oxide. Preferred polyalkylene polyether polyols are polypropylene polyether polyols and those which contain 5 to 25 mols % (based on the total quantity of alkylene oxide) of terminal ethylene oxide units. In the mixtures used according to the invention it is particularly preferred to use linear polypropylene polyether glycols within a molecular weight range of from 300 to 1999 and particularly from 400 to 999 optionally containing 5 to 25 mole %, based on the total quantity of alkylene oxide, of terminal ethylene oxide units, as the sole polyalkylene polyether polyol component. These are distinguished by a rapid and uniform reaction.

The diisocyanatodiurethanes mentioned under 2a) are compounds of the general formula:



in which R has the meaning given above.

These diisocyanotodiurethanes may be obtained in known manner by reacting at least 2 mols of 4,4'-diisocyanatodiphenylmethane with 1 mol of a low molecular weight (62—400) glycol. The preparation of the diisocyanatodiurethanes is preferably carried out by gradually adding 1 mol of the given glycol to 2 to 10 mols, preferably 4 to 6 mols, of 4,4'-diisocyanatodiphenylmethane. When more than 2 mols of aromatic diisocyanate are used per mol of glycol, a mixture of the diisocyanatodiurethane and excess aromatic diisocyanate is obtained. The reaction between the glycol and 4,4'-diisocyanatodiphenylmethane is preferably carried out at a temperature of from 20 to 100°C, in particular from 50 to 85°C.

Glycols suitable for preparing the diisocyanatodiurethanes are those within the

molecular weight range of from 62 to 400, for example ethylene glycol, propylene glycol, butylene glycol, butane-2,3-diol, diethylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, dipropylene glycol, tripropylene glycol, tetrapropylene glycol, pentapropylene glycol, dibutylene glycol and tributylene glycol. The corresponding polypropylene glycols are preferably used, in particular tripropylene glycol.

The reaction product of 4 to 6 mols of 4,4'-diisocyanatodiphenylmethane and 1 mol of polypropylene glycol, especially tripropylene glycol, is distinguished by being particularly easily processed. The reaction product then consists of a mixture of 1 mol of diisocyanatodiurethane and 2 to 4 mols of excess 4,4'-diisocyanatodiphenylmethane.

To prepare the adhesive mixtures used according to the invention, the polyether component which consists of one or more polyethers of the type mentioned under 1a) or a mixture of two or more polyethers of the type mentioned under 1a) and 1b) is mixed with a quantity of diisocyanate components 2a) and 2b) such that the resulting NCO/OH ratio is 0.5 to 2.5, preferably 0.7 to 2.0.

If the adhesives used in the present bonding process are not required to satisfy any particular requirements, especially as regards colour, then the known crude polyisocyanate mixture containing 30 to 70%, by weight, of 4,4'-diisocyanatodiphenylmethane, which is obtainable by the phosgenation of aniline/formaldehyde condensates, may be used instead of 4,4'-diisocyanatodiphenylmethane as component 2b) or for preparing component 2a).

Component 3 in the adhesive mixtures used according to the invention consists of any of the conventional catalysts for accelerating the NCO/OH reaction, in particular tertiary amines, such as 1,4-diaza-bicyclo-(2,2,2)-octane, N,N'-dimethylpiperazine or organic metal compounds, in particular tin compounds, such as dibutyl tin dilaurate. The catalysts are added in quantities of from 0.01 to 5, preferably from 0.1 to 3%, by weight, based in the total quantity of components 1a), 1b), 2a) and 2b).

The mixed adhesive used has a relatively low viscosity immediately after it has been mixed and some time thereafter, and during that time can easily be applied with a simple implement, such as a brush, or a two-component dosing device to the materials which are to be bonded together, such as paper, textiles, synthetic resins, rubber, metal or ceramics. The adhesive subsequently solidifies and attains its maximum bonding power within a short time.

Natural or synthetic resins, age resistors, pigments and fillers may be added to modify the adhesive used according to the invention.

If the adhesives used contain small quantities of water, products, such as sodium aluminosilicate (zeolite), for example may be added to prevent foaming.

The invention will now be further described with reference to the following Examples.

Example 1

100.0 Parts, by weight, of a polypropylene ether triol of hydroxy number 370 which had been started on trimethylolpropane, 124.0 parts, by weight, of the diisocyanato diurethane prepared by reacting 5 molar parts of 4,4'-diisocyanatodiphenylmethane with 1 molar part of tripropylene glycol, and 1.0 part, by weight, of 1,4-diazabicyclo-(2,2,2)-octane were stirred together. Immediately after stirring, the mixture was used for bonding an aluminium-copper-magnesium alloy.

Pretreatment of the samples was carried out in accordance with DIN 53281, Sheet 1, and preparation of the samples according to DIN 53281, Sheet 2. The adhesive mixture was applied to both the overlapping aluminium surfaces with a brush. The quantity of adhesive used was about 250 g/m². The bonds were then fixed by application of a pressure of 1 kp/cm² for 5 minutes and the bond strength determined in accordance with DIN 53283.

The bond strengths obtained after the given times were as follows:

5 minutes	79 kp/cm ²
10 minutes	125 kp/cm ²
15 minutes	128 kp/cm ²
30 minutes	110 kp/cm ²
24 hours	115 kp/cm ²

Example 2

30.0 Parts, by weight, of a polypropylene ether diol (hydroxyl number 115) which had been started on propane-1,2-diol, 70.0 parts, by weight, of a polypropylene ether triol (hydroxyl number 370) which had been started on trimethylolpropane, 98.0 parts,

by weight, of the diisocyanatodiurethane prepared by reacting 5 molar parts of 4,4'-diisocyanatodiphenylmethane with 1 molar part of tripropylene glycol, and 1.0 part, by weight, of 1,4-diaza-bicyclo-(2,2,2)-octane were stirred together. Immediately after stirring, the mixture was used for bonding an aluminium-copper magnesium alloy as described in Example 1.

The bond strengths obtained after the given times were as follows:

	5 minutes	43 kp/cm ²	
	10 minutes	93 kp/cm ²	
	15 minutes	130 kp/cm ²	
10	30 minutes	135 kp/cm ²	10
	24 hours	120 kp/cm ²	

Example 3

50.0 Parts, by weight, of a polypropylene ether diol (hydroxyl number 115) which had been started on propane 1,2-diol, 50.0 parts, by weight, of a polypropylene ether triol (hydroxyl number 370) which had been started on trimethylol propane, 81.0 parts, by weight, of the diisocyanatodiurethane prepared by reacting 5 molar parts of 4,4'-diisocyanatodiphenylmethane with 1 molar part of tripropylene glycol, and 1.0 part, by weight, of 1,4-diaza-bicyclo-(2,2,2)-octane were stirred together. Immediately after stirring, the mixture was used for bonding the aluminium alloy as described in Example 1.

The bond strengths obtained after the given times were as follows:

	5 minutes	48 kp/cm ²	
	10 minutes	65 kp/cm ²	
	15 minutes	48 kp/cm ²	
25	30 minutes	130 kp/cm ²	25
	24 hours	225 kp/cm ²	

Example 4

80.0 Parts, by weight, of a polypropylene ether triol (hydroxyl number 370) which had been started on trimethylolpropane and 20.0 parts, by weight, of a polypropylene ether triol (hydroxyl number 39.0) which had been started on trimethylolpropane and contained 9.2 mols % of terminal ethylene oxide units, 99.0 parts, by weight, of the diisocyanatodiurethane prepared by reacting 5 molar parts of 4,4'-diisocyanatodiphenylmethane with 1 molar part of tripropylene glycol and 1.0 part, by weight, of 1,4-diaza-bicyclo-(2,2,2)-octane were stirred together. Immediately after stirring, the mixture was used for bonding the aluminium alloy as described in Example 1.

The bond strengths obtained after the given times were as follows:

	5 minutes	70 kp/cm ²	
	10 minutes	83 kp/cm ²	
40	15 minutes	85 kp/cm ²	40
	30 minutes	235 kp/cm ²	
	24 hours	210 kp/cm ²	

Example 5

50.0 Parts, by weight, of a polypropylene ether diol (hydroxyl number 115) which had been started on propane-1,2-diol, 50.0 parts, by weight, of a polypropylene ether triol (hydroxyl number 370) which has been started on trimethylolpropane, 100.0 parts, by weight, of the diisocyanatodiurethane which had been prepared by reacting 5 molar parts of 4,4'-diisocyanatodiphenylmethane with 1 molar part of tripropylene glycol, and 2.0 parts, by weight, of N,N'-dimethylpiperazine were stirred together. Immediately after stirring, the mixture was used for bonding aluminium alloy as described in Example 1.

The bond strengths obtained after the given times were as follows:

	5 minutes	2 kp/cm ²	
	10 minutes	3 kp/cm ²	
55	15 minutes	7 kp/cm ²	55
	30 minutes	51 kp/cm ²	
	24 hours	120 kp/cm ²	

Example 6
(For Comparison Purposes Only)

50.0 Parts, by weight, of a polypropylene ether diol (hydroxyl number 115) which had been started on propane-1,2-diol, 50.0 parts, by weight, of a polypropylene ether triol (hydroxyl number 370) which had been started on trimethylol propane, 770 parts, by weight, of polyisocyanate prepared by the condensation of aniline and formaldehyde followed by phosgenation with the elimination of hydrochloric acid, and 2.0 parts, by weight, of N,N'-dimethylpiperazine were stirred together. Immediately after stirring, the mixture was used for bonding aluminium alloy as described in Example 1.

The bond strength obtained after the given times were as follows:

15 minutes	4 kp/cm ²
30 minutes	12 kp/cm ²
60 minutes	30 kp/cm ²
24 hours	81 kp/cm ²

Example 7

80.0 Parts, by weight of a polypropylene ether diol (hydroxyl number 115) which had been started on propane-1,2-diol, 20.0 parts, by weight, of a polypropylene ether triol (hydroxyl number 370) which had been started on trimethylolpropane, 58.6 parts, by weight, of the diisocyanatodiurethane prepared by reacting 5 molar parts of 4,4'-diisocyanatodiphenylmethane with 1 molar part of tripropylene glycol, and 0.2 parts, by weight, of 1,4-diaza-bicyclo-(2,2,2)-octane were stirred together.

Immediately after stirring, the adhesive was applied to a 40 μ aluminium foil by means of a coating knife (approximately 7 g/m²), and a 50 μ polyterephthalic acid ester foil was immediately pressed on it with the aid of two rubber rollers at room temperature. The strengths of the bonds were subsequently determined by the peeling test at 20°C. (tearing speed: 100 mm/min., tearing angle 90°) in terms of p per 15 mm of tearing width.

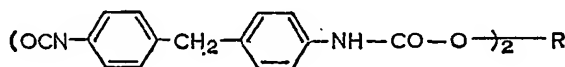
Bond strengths after

30 minutes	60 p/15 mm
60 minutes	300 p/15 mm
360 minutes	580 p/15 mm
24 hours	640 p/15 mm

WHAT WE CLAIM IS:—

1. A process for bonding together materials in which a mixed adhesive which comprises a mixture of:

- 1) (a) at least one polyalkylene polyether polyol having a molecular weight of from 300 to 1999;
- (b) from 0 to 150 mols %, based on component 1a, of at least one polyalkylene polyether polyol having a molecular weight of from 2000 to 6000;
- 2) (a) at least one diisocyanatodiurethane corresponding to the following general formula:



wherein R represents a radical obtained by removing the hydroxyl groups from a glycol which glycol has a molecular weight of from 62 to 400;

- (b) 0—800 mols %, based on component 2a, of 4,4'-diisocyanatodiphenylmethane; and

3) a catalyst for accelerating the OH/NCO reaction; the ratio of 1(a)+(b) to 2(a)+(b) corresponding to an NCO/OH ratio of from 0.5 to 2.5, is applied to the material and the bonds are fixed by the application of pressure.

2. A process as claimed in Claim 1, in which the adhesive component 1(a) has a molecular weight of from 400 to 999.

3. A process as claimed in Claim 1 or Claim 2 in which the polyol component (1) of the adhesive consists solely of the component 1(a).

4. A process as claimed in Claim 1 or Claim 2 in which the adhesive component 1(b) has a molecular weight of from 2500 to 4000.

5. A process as claimed in any of Claims 1 to 4, in which the polyol in the adhesive is obtained by reacting an alkylene oxide with a suitable starter molecule.
6. A process as claimed in Claim 5 in which the alkylene oxide is ethylene oxide, propylene oxide or butylene oxide.
- 5 7. A process as claimed in Claim 5 or Claim 6 in which the starter molecule is an amine, water or an alcohol which is at least dihydric and has a molecular weight of from 62 to 400. 5
8. A process as claimed in any of Claims 1 to 3, or 5 to 7, in which the adhesive polyol component 1) is a linear polypropylene polyether glycol which may contain from 5 to 25 mol %, based on the total quantity of alkylene oxide, of terminal ethylene oxide units. 10 10
9. A process as claimed in any of Claims 1 to 8, in which the diisocyanatodiurethane component 2a of the adhesive is obtained by reacting at least two mols of 4,4'-diisocyanatodiphenylmethane with 1 mol of a glycol having a molecular weight of from 62 to 400. 15 15
10. A process as claimed in Claim 9, in which the diisocyanatodiurethane is prepared by adding, gradually, 1 mol of the given glycol to from 2 to 10 mols of 4,4'-diisocyanatodiphenylmethane.
11. A process as claimed in Claim 10, in which 1 mol of glycol is added to from 4 to 6 mols of 4,4'-diisocyanatodiphenylmethane. 20 20
12. A process as claimed in any of Claims 9 to 11 in which the glycol and the 4,4'-diisocyanatodiphenylmethane are reacted together at a temperature of from 20 to 100°C.
13. A process as claimed in Claim 12 in which the glycol and the 4,4'-diisocyanatodiphenylmethane are reacted together at a temperature of from 50 to 85°C. 25 25
14. A process as claimed in any of Claims 1 to 13, in which the glycol used in the preparation of the diisocyanatodiurethane component 2(a) of the adhesive is a polypropylene glycol.
15. A process as claimed in Claim 14 in which the glycol is tripropylene glycol. 30 30
16. A process as claimed in any of Claims 1 to 15, in which the ratio of components 1(a)+(b) to 2(a)+(b) of the adhesive is such that the resulting NCO/OH ratio is from 0.7 to 2.0.
17. A process as claimed in any of Claims 1 to 16, in which the 4,4'-diisocyanatodiphenyl methane used as component 2(b) of the adhesive and/or in the preparation of component 2(a) of the adhesive is replaced by the crude polyisocyanate mixture obtained by the phosgenation of aniline/formaldehyde condensates. 35 35
18. A process as claimed in any of Claims 1 to 17, in which the catalyst for accelerating the NCO/OH reaction, the adhesive component (3), is a tertiary amine or an organic metal compound.
19. A process as claimed in any of Claims 1 to 18, in which the catalyst concentration in the adhesive is from 0.01 to 5%, by weight, based on the total quantity of adhesive components 1 and 2. 40 40
20. A process as claimed in Claim 19 in which the catalyst concentration is between 0.1 and 3%, by weight.
21. A process as claimed in any of Claims 1 to 20, in which the adhesive also contains natural or synthetic resins, age resistors, pigments and/or fillers. 45 45
22. A process as claimed in any of Claims 1 to 21, in which the adhesive is applied by means of a brush or a two-component dosing device.
23. A process as claimed in any of Claims 1 to 22, in which the substrate is paper, a textile, a synthetic resin, rubber, a metal or a ceramic. 50 50
24. A process as claimed in Claim 1 substantially as herein described.
25. A process as claimed in Claim 1 substantially as herein described with reference to any one of the Examples.
26. Materials when bonded by a process as claimed in any of Claims 1 to 25.

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